



Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

XXIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON TETRABROMDINITROBENZOL.

BY C. LORING JACKSON AND W. D. BANCROFT.

Presented May 28, 1889.

AFTER it had been determined that the tribromdinitrobenzol, melting at 192° , reacted easily with a variety of substances, it seemed of interest to try similar experiments with a tetrabrom compound, and we selected for this purpose the tetrabromdinitrobenzol, melting at 228° , and describe in this paper the results of our work, which may be briefly summarized as follows. Tetrabromdinitrobenzol is not acted on by alcoholic ammonia in open vessels, but, if heated with it in a sealed tube, is converted into a yellow substance insoluble in all the common solvents, which seems to be the bromtriamidodinitrobenzol. With aniline the bromtrianilidodinitrobenzol, melting at 175° – 176° , is formed. With sodium malonic ester it gives in the cold dibromdinitrophenylmalonic ester, melting point 89° , which possesses acid properties forming a red sodium salt, and is converted by aniline into the bromanilidodinitrophenylmalonic ester, melting at 127° . The action of these reagents on the tetrabromdinitrobenzol is therefore similar to their behavior with tribromdinitrobenzol, the fourth atom of bromine remaining unaffected in all these reactions. We were prevented by want of time from trying to remove this fourth atom of bromine by reactions carried on at higher temperatures. We have studied also the reduction of the dibromdinitrophenylmalonic ester with tin and hydrochloric acid, and have obtained in this way the bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$, melting at about 212° , and its chloride, $C_6H_2BrNH_2(CH_2CONH)HClH_2O$. We may add, that in preparing the tetrabromdinitrobenzol from somewhat impure tetrabrombenzol we obtained the as yet undescribed pentabromnitrobenzol, which melts at 248° , and on another occasion the hexabrombenzol.

Preparation of Tetrabromdinitrobenzol.

Our starting point in the manufacture of the tetrabrombenzol was tribromaniline, which we prepared as follows. 60 grs. of aniline were dissolved in dilute hydrochloric acid, and the solution, having been made up to a volume of about three litres, a rapid stream of air saturated with bromine vapor was sucked through it by means of a Bunsen pump, until the liquid assumed a distinct yellow color. The precipitate of tribromaniline was then removed by straining through cheesecloth, washed with a stream of common water until free from acid, when the greater part of the water was squeezed out with a screw press, and the product thoroughly dried on a steam radiator. In this way a quantitative yield of tribromaniline free from colored by-products was obtained at a much less expense of time and labor than by the method formerly in use.

To convert the tribromaniline into tetrabrombenzol we used the method of V. von Richter* slightly modified, which left nothing to be desired so far as the yield was concerned, when the process was successful; this, however, was not always the case, as frequently the product was a substance melting in the neighborhood of 87° , from which tetrabrombenzol melting at 98° could be obtained only by repeated crystallization from a mixture of alcohol and benzol, and even then not in large quantity.† In spite of many experiments, we have not succeeded in determining with certainty the conditions under which this mixture was formed, or the nature of the impurity which it contained, and can give only the conditions which usually gave a good result. 25 grs. of the tribromaniline were dissolved in a small quantity of glacial acetic acid with the aid of heat, and, after the solution had cooled, a concentrated aqueous solution of hydrobromic acid ‡ was added, which threw down a precipitate of tribromaniline bromide; the mixture was stirred vigorously, and, disregarding the precipitate, a concentrated aqueous solution of about the theoretical amount of sodic nitrite added in small portions, keeping the solution cool by immersing the beaker containing it in cold water; the beaker was then warmed gently on the water bath, and solid sodic nitrite added in small pieces

* Ber. d. ch. G., viii. 1428.

† Owing to this uncertainty in our modification of Von Richter's process, we made two attempts to use Sandmeyer's method, but encountered such difficulties in applying it to tribromaniline that we decided it was easier to prepare our material by Von Richter's process than to overcome these difficulties.

‡ An attempt to substitute potassic bromide and sulphuric acid for hydrobromic acid gave a much poorer yield; less than 50 per cent instead of 90.

until the proportion of the total sodic nitrite to the tribromaniline was three molecules to one (this very large excess of sodic nitrite being found necessary to complete the reaction). The liquid on cooling deposited a tarry mass, which was extracted repeatedly with small quantities of hot alcohol, until it was converted into crystals (melting at about 95°). An additional amount of these crystals was obtained by pouring into water the red liquid from which the tar had been deposited, but this amount was not large. The product, after purification by one or two crystallizations from hot alcohol, showed a yield of from 89 to 93 per cent of the theoretical.

To convert the tetrabrombenzol into tetrabromdinitrobenzol, 10 grs. of it were dissolved with the aid of heat in nitric acid of specific gravity 1.52, prepared in the laboratory from nitre and sulphuric acid; then the same volume of strong sulphuric acid was added, about 200 c.c. of the mixture of the two acids being used, and, after standing in the cold for ten minutes, the whole was boiled for about an hour in a flask closed with a glass bulb. If the tetrabrombenzol was sufficiently pure there was little foaming and no violent action, and on cooling a white crystalline solid separated, which was nearly pure tetrabromdinitrobenzol, and, after crystallization from benzol with a little alcohol, or from chloroform, showed the right melting point 228° .*

If, on the other hand, a tetrabrombenzol was used containing some of the impurity already mentioned, which, when present in quantity, lowered the melting point to the neighborhood of 87° , the action was violent, the boiling being accompanied by much foaming, the product was often oily, and, after most of the solid had been precipitated by water, the aqueous liquid contained decomposition-products, as was shown by the blackish precipitate formed in it on the addition of sodic carbonate. The main product in this case was a mixture of the tetrabromdinitrobenzol and another substance, which was obtained by treatment with aniline or sodium malonic ester, and subsequent separation of the derivative of the tetrabromdinitrobenzol by crystalliza-

* One of us and J. F. Wing (These Proceedings, xxiii. 148) some years ago obtained tetrabromdinitrobenzol as a secondary product in the manufacture of tribromtrinitrobenzol, but we were unable to raise its melting point above 224° ; this was ascribed at the time to the presence of a little tribromtri- (or di-) nitrobenzol, an opinion which is confirmed by the fact mentioned above that tetrabromdinitrobenzol prepared by us according to the usual method showed the melting point 228° given by Von Richter (Ber. d. ch. G., 1875, p. 1427). The difficulty in removing the tribrom compound can be accounted for by supposing that it forms the addition-product observed by one of us and G. D. Moore (Ber. d. ch. G. 1888, p. 1707), or an analogous one with the trinitro compound.

tion out of alcohol from the unaltered second product, which was then purified by crystallization from boiling alcohol, or better chloroform, until it showed the constant melting point 248° , when, after drying at 100° , it was analyzed with the following results: —

- I. 0.1711 gr. of the substance gave on combustion 0.0855 gr. of carbonic dioxide and 0.0151 gr. of water.
- II. 0.2100 gr. of the substance gave 0.1075 gr. of carbonic dioxide and 0.0103 gr. of water.
- III. 0.1846 gr. of the substance gave 3.5 c.c. of nitrogen at a temperature of 17° and a pressure of 773 mm.
- IV. 0.1881 gr. of the substance gave, according to the method of Carius, 0.3418 gr. of argentic bromide.

	Calculated for $C_6Br_5NO_2$.	I.	II.	Found. III.	IV.
Carbon	13.90	13.63	13.96		
Hydrogen	0.00	0.98	0.54		
Nitrogen	2.70			2.24	
Bromine	77.23				77.34

There can be no doubt, therefore, that this is the as yet undescribed pentabromnitrobenzol.

Properties. — The pentabromnitrobenzol crystallizes in very slender little white needles, which melt at 248° . The substance is essentially insoluble in water or ligroine; nearly insoluble in cold ethyl or methyl alcohol, more soluble when hot, but still sparingly; the solubility in glacial acetic acid or acetone is similar, except that it is much more soluble in either of these solvents when hot than it is in alcohol; readily soluble in hot benzol or chloroform; very soluble in ether or carbonic disulphide.

Although pentabromnitrobenzol was the usual impurity, on one occasion a different product was obtained, which consisted of small needles melting, after crystallization from benzol, at about 312° , essentially insoluble in alcohol or sodic hydrate, and containing no nitrogen. We inferred therefore that this was the hexabrombenzol, which is said to melt above 315° , and to be almost insoluble in boiling alcohol, and this inference was proved to be correct by the following analysis: —

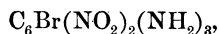
0.1303 gr. of the substance gave, by the method of Carius, 0.2666 gr. of argentic bromide.

	Calculated for C_6Br_6 .	Found.
Bromine	86.96	87.10

Preliminary Experiments.

After the tetrabromdinitrobenzol had been prepared, the following experiments were tried to determine the ease with which it reacted with various substances.

As has been stated in an earlier paper, alcoholic ammonia has no action on tetrabromdinitrobenzol in the cold, or even if the substances are heated together in open vessels. If however the mixture is heated to 100° in a sealed tube for four or more hours, a reaction takes place giving an orange precipitate and a red alcoholic solution in addition to some unaltered tetrabromdinitrobenzol. The orange insoluble substance was undoubtedly the bromtriamidodinitrobenzol, but, as it was insoluble in all the common solvents, we could only try to purify it by washing, and even after repeated treatment with water, alcohol, chloroform, and benzol were unable to obtain a substance giving constant results on analysis; the bromine varied in different samples from 25.34 to 29.07 per cent, the amount required by the formula,



being 27.39. Although it is probable that further work on this substance would have enabled us to find a method of purifying it, we did not think it worth while to sacrifice the time, as these analyses show that the reaction has run in the same way as that between tribromdinitrobenzol and alcoholic ammonia, and nothing of interest was likely to be found in its investigation. The substance is an orange-yellow powder, insoluble in all the common solvents, and not melting even at 285°. The alcoholic filtrate contained a yellow substance melting at 185° in the crude state, but we did not obtain enough of it for investigation. With aniline a more favorable result was obtained, which is described fully in the next section of this paper.

When boiled with potassic sulphocyanate in alcoholic solution in a flask with a return condenser, there was very little action, but, if amyl alcohol was substituted for ethyl alcohol, so that the action would take place at a higher temperature, a dark red substance was formed insoluble in all the common solvents. In this respect the tetrabromdinitrobenzol behaved exactly like the tribromdinitrobenzol, and, as it had been found impossible to purify the corresponding product from the tribrom compound, we did not think it worth while to continue work in this direction.

With sodium malonic ester or sodium acetacetic ester it behaves like the tribromdinitrobenzol. The action with sodium malonic ester is described in detail later in this paper.

In all the derivatives of tetrabromdinitrobenzol which were analyzed it was found that only three of the atoms of bromine had been attacked. We had hoped to try some experiments at higher temperatures for the purpose of replacing the fourth atom of bromine, but the work described in this paper has taken so much time that we have been unable to take up this branch of the subject.

Bromdinitrotrianilidobenzol, $C_6Br(NO_2)_2(C_6H_5NH)_3$.

To prepare this substance tetrabromdinitrobenzol was heated with aniline in the proportion of one molecule of the former to a little more than six of the base. Convenient amounts were 7 grs. of tetrabromdinitrobenzol to 8.3 grs. of aniline. When the mixture was heated on the water bath, the solid dissolved after some time, the solution being accompanied by a change of color from yellow to bright red, and on cooling the whole solidified to a mass of red needles; but in order to get even a tolerable yield of the new substance the heating on the water bath must be continued for at least four to six hours, and then it is not by any means complete. A higher heat than the water bath should not be used, as then the mixture shows a tendency to pass into a purplish coloring matter, resembling impure rosaniline in appearance, and similar to the substance obtained in the same way from tribromdinitrobenzol,* and like that undoubtedly produced by the nitro groups taking part in the reaction. If the reaction had run properly, the product consisted of a viscous or crystalline mass of the color of red lead, from which in the first place the aniline bromide and excess of aniline were removed by washing with water containing a little hydrochloric acid, leaving a brick-red powder. The purification was completed by crystallization from alcohol, and afterward from a mixture of alcohol and chloroform, until it showed the constant melting point 175° – 176° . If there was difficulty in obtaining crystals of the proper melting point, it was found advisable to warm the substance again with aniline for two or more hours, and then purify again in the manner just described. In addition to unaltered tetrabromdinitrobenzol a small amount of an impurity was found, which melted in the crude state between 120° and 140° , but we did not succeed in isolating a substance fit for analysis from it. The main product, when pure, was dried at 100° , and analyzed with the following results:—

- I. 0.1667 gr. of the substance gave 20.4 c.c. of nitrogen at a temperature of 25° and a pressure of 768.4 mm.

* These Proceedings, xxiii. 145.

II. 0.1624 gr. of the substance gave, by the method of Carius, 0.0578 gr. of argentic bromide.

	Calculated for	Found.	
	$C_6Br(NO_2)_2(C_6H_5NH)_3$.	I.	II.
Nitrogen	13.46	13.81	
Bromine	15.38		15.15

Properties.—Bromtrianilidodinitrobenzol forms a brilliant but rather dark red crystalline powder, which, when examined with the microscope, consists of crystals of two forms, rather short prisms terminated by an obtuse angle, and thick groups shaped like an hour-glass and made up of short prisms, which seem to have the same terminal angles as those which are not in groups; the groups are rather darker in color than the free prisms, but this is probably due to their being thicker. When crystallized from hot alcohol, instead of the usual mixture of alcohol and chloroform, characteristic forms like sheaves were obtained, also a small quantity of red nearly square plates. It melts at 175° – 176° ; is essentially insoluble in ligroine, or in water either cold or boiling; very slightly soluble in cold alcohol, more soluble in hot; more soluble in methyl than in ethyl alcohol; slightly soluble in cold ether, freely in hot; moderately soluble in glacial acetic acid; freely soluble in benzol, chloroform, or carbonic disulphide; very freely in acetone. The best solvent for it is a mixture of alcohol and chloroform, as it tends to separate in a viscous state from the solution in chloroform alone. Strong sulphuric acid dissolves it slightly, forming a pale yellow solution. Strong nitric acid acts in the same way, but less energetically; fuming nitric acid acts upon it violently even in the cold. Hydrochloric acid has no action either hot or cold. The absence of basic properties is accounted for by the presence of the two nitro groups. We tried also the action of sodic hydrate, as certain nitroamido compounds possess weak acid properties,—for instance, the trinitrotoluidine of Nölting and Salis,*—but found that it produced no effect.

Dibromdinitrophenylmalonic Ester, $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$.

This substance was prepared by acting on one molecule of tetrabromdinitrobenzol with about four molecules of sodium malonic ester, as follows: 15 grs. of tetrabromdinitrobenzol dissolved in about 20–30 c.c. of benzol were mixed with 20 grs. of malonic ester previously converted into sodium malonic ester by treatment with the sodic ethyl-

* Ber. d. ch. G., xv. 1864.

ate made from 3 grs. of sodium dissolved in 100 to 150 c.c. of absolute alcohol. The action began at once, as shown by the appearance of a dark red color and a considerable evolution of heat, so that the flask became too hot to hold in the hand with comfort; in this respect it differed from that with the tribromdinitrobenzol, as, although in that case the red color appeared at once, no perceptible rise of temperature was observed in any part of the reaction. To make certain that the reaction had run as far as possible, the mixture was allowed to stand in the cold for three or four days. At the end of this time the product was diluted with about half a litre of water, and the benzol separated from the red aqueous solution of the salt of the new substance. Upon adding dilute sulphuric acid to this aqueous solution, the new substance was precipitated, and after washing with water was purified by crystallization from alcohol until it showed the constant melting point 89° , when it was dried *in vacuo* for analysis. The benzol solution, which separated on the addition of water, was evaporated to dryness, and the residue, consisting of the new substance, a little unaltered tetrabromdinitrobenzol, and an oil, after being freed from the oil on the pump, was treated with alcohol, in which the tetrabrom compound is essentially insoluble, and the small amount of the new substance thus obtained was added to that from the aqueous solution.

- I. 0.2183 gr. of the substance gave on combustion 0.2568 gr. of carbonic dioxide and 0.0528 gr. of water.
- II. 0.2144 gr. of the substance gave 11.4 c.c. of nitrogen at a temperature of $23^{\circ}.1$ and a pressure of 763.4 mm.
- III. 0.2372 gr. of the substance gave, by the method of Carius, 0.1833 gr. of argentic bromide.

	Calculated for $C_6HBr_2(NO_2)_2CH(CO_2C_2H_5)_2$.	I.	Found. II.	III.
Carbon	32.23	32.07		
Hydrogen	2.48	2.69		
Nitrogen	5.78		6.02	
Bromine	33.06			32.91

The yield of dibromdinitrophenylmalonic ester was very satisfactory. On one occasion 5 grs. of tetrabromdinitrobenzol gave 4 grs. of the dibromdinitrophenylmalonic ester, instead of the 5 grs. required by the theory, that is, 80 per cent of the theoretical yield. This large yield proves conclusively that dibromdinitrophenylmalonic ester is the only aromatic product of the reaction, a point which before this observation seemed somewhat doubtful in the analogous preparations described in

other papers from this laboratory, as in them the yield rose but little above 50 per cent of the theory.

The amount of bromine separated as bromide of sodium in the preparation of the substance was determined in two cases as follows:—

- I. 5 grs. of tetrabromdinitrobenzol yielded 3.707 grs. of argentic bromide, corresponding to 1.578 grs. of bromine.
- II. 5 grs. of tetrabromdinitrobenzol yielded 3.631 grs. of argentic bromide, corresponding to 1.545 grs. of bromine.

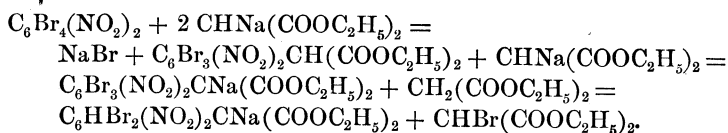
The theoretical yield, if two of the atoms of bromine had been removed, would be 1.653 grs.

Percentage of bromine found as bromide of sodium, —

I.	II.
95.43	93.48

From these numbers it appears that essentially all the bromine is removed as sodic bromide.

The oil which formed the secondary product of the reaction was not investigated further, as from the composition of the ester, and the fact that all the bromine appeared as sodic bromide, there could be no question that the nature of this action is the same as that with the tri-brom compounds; and in those cases* the study of the oils has shown conclusively the mode of formation of the substances. There can be no doubt, therefore, that the reactions which take place in this case should be written as follows:—



The brommalonic ester being converted afterward into tartronic or acetylentetracarbonic ester.

Properties.—The dibromdinitrophenylmalonic ester crystallizes from alcohol usually in slightly yellow to colorless needles, which unite into groups like pompons if the solution is dilute; seen under the microscope they consist of rather long rhombic plates with a decidedly acute angle, about six times as long as their breadth, or even slenderer, either free or in radiating groups, the crystals branching so as to give the effect of being arranged in curved lines. When less well developed, the groups are made up of fine needles very much

* These Proceedings, xxiv. 238, 265.

branched, like certain feathery seaweeds. From the oil which forms the secondary product in its preparation, the substance crystallizes in flattened prisms, often two centimeters in length, arranged in slightly radiating groups. The melting point is 89° . It is essentially insoluble in water or ligroine; slightly soluble in cold, freely in hot methyl, or ethyl alcohol; freely soluble in carbonic disulphide, glacial acetic acid, or acetone; very freely in ether, benzol, or chloroform. Strong sulphuric acid has little, if any, action on it in the cold, but dissolves it slightly without change of color when hot. Strong nitric acid also seems not to act upon it in the cold, but, when warmed with it, turns yellow and imparts a yellow color to the drops of the melted substance which swim on its surface. Hydrochloric acid does not seem to act on it in open vessels either cold or warm, although from analogy with the corresponding monobrom compound it is fair to suppose that it would decompose it if the two substances were heated to 150° in a sealed tube.

The dibromdinitrophenylmalonic ester has well marked acid properties, as was to be expected from the fact that one of its atoms of hydrogen is attached to a carbon atom in direct contact with two carboxylester radicals and a dinitrophenyl. An excess of sodic hydrate in aqueous solution has but little action on the solid, turning it pale red; if, however, a drop of alcohol is added, it turns a very dark red at once, and the salt begins to dissolve. Potassic carbonate acts in much the same way. Acid sodic carbonate in aqueous solution has no effect, but if alcohol is added there is a slight action shown by formation of a little of the red salt. Ammonic hydrate in aqueous solution has but little action, but turns red if a little alcohol is added, and upon warming this mixture a deep brownish red solution is obtained, which smells strongly of ammonia, even if an excess of the ester is used in making it. It seemed to be decomposed by heating, or by exposure to the air, so that the ammonium salt must be a very unstable substance. The solution of the ammonium salt made with an excess of the ester (but still smelling of ammonia) was treated with various reagents, and gave the following characteristic precipitates:—

With a salt of *magnesium, calcium, strontium, or barium*, very heavy pale red flocks.

With a *zinc* salt, pale yellow flocks.

With a salt of *manganese, cobalt, or nickel*, pale red flocks.

With a *ferric* salt, pale brownish purple.

With a *cupric* salt, bright yellow.

With salts of *mercury*, pale red.

With a *cadmium* salt, reddish yellow.

With a *lead* salt, whitish red.

With a *silver* salt, pale orange.

Strong nitric acid gave with the salts a white precipitate, probably the unaltered ester. In this respect it differs from bromtrinitrophenylmalonic ester.

Bromanilidodinitrophenylmalonic Ester,
 $\text{C}_6\text{HBr}(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_2\text{CH}(\text{COOC}_2\text{H}_5)_2$.

This substance was made by adding aniline to the dibromdinitrophenylmalonic ester in the proportion of a little more than two molecules of the base to one of the ester. The reaction began in the cold, but was brought to an end by warming the mixture for a short time on the water bath. The product, after washing with water, to which a little hydrochloric acid was added to remove aniline bromide and the excess of aniline, was crystallized from hot alcohol, until it showed the constant melting point 127° , when it was dried at 100° , and analyzed with the following result:—

0.2003 gr. of the substance gave 14.85 c.c. of nitrogen at a temperature of $20^\circ.5$ and a pressure of 762 mm.

	Calculated for $\text{C}_6\text{HBr}(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_2\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$.	Found.
Nitrogen	8.47	8.49

Properties.—The bromanilidodinitrophenylmalonic ester crystallizes from alcohol in bright red needles, which under the microscope are seen to be slender prisms terminated usually by two planes, less commonly by one, and seeming to belong to the monoclinic system. The substance melts at 127° ; and is essentially insoluble in cold water, very sparingly soluble in boiling water, as shown by the faint yellow color imparted to the liquid; insoluble in ligroine; very slightly soluble in cold ethyl or methyl alcohol, more freely in either of these solvents when hot; slightly soluble in ether; soluble in benzol or glacial acetic acid; freely soluble in chloroform, carbonic disulphide, or acetone. Strong sulphuric acid dissolves it slightly, forming a yellowish solution; the solubility did not seem to be increased by heat. Strong nitric acid dissolved it rather more freely than sulphuric acid, and the solubility was increased by heat. Strong hydrochloric acid had no action upon it, although it is probable that long heating in a sealed tube with this acid would have decomposed it in the way described* under the bromdinitrophenylmalonic ester.

* These Proceedings, xxiv. 240.

The acid properties of this substance have been much weakened by the replacement of bromine by the basic aniline radical C_6H_5NH , but that they still exist is shown by the following observations. Sodic hydrate in aqueous solution has no action on the solid, but on the addition of a little alcohol a dark red solution of the salt is formed; sodic carbonate in aqueous solution produces no effect, but on the addition of alcohol a very slight red coloration appears; acid sodic carbonate produces no effect even in presence of alcohol. Ammonic hydrate in aqueous solution does not dissolve the solid substance, and, even if alcohol is added, the action is very slight; if, however, the mixture of aqueous ammoniac hydrate, alcohol, and the solid is warmed on the water bath, a dark red solution is obtained, which smells of ammonia, even if a large excess of the ester is used. The behavior of such a solution with various reagents was studied with the following results:—

Salts of *magnesium, calcium, strontium, or barium* gave rusty brown precipitates.

The salts of the heavy metals gave yellow precipitates, except where the color was modified by the excess of ammonia which could not be removed from the solution of the salt.

Reduction of Dibromdinitrophenylmalonic Ester.

The investigation of this subject interested us especially, because it seemed probable that the diamidophenylmalonic or acetic acid, which would be the first product of the reaction, would lose water and become converted into an amidooxindol, especially since Bischoff* obtained from the reduction of his orthonitrobenzoylmalonic ester α - γ -dihydroxychinoline. As with zinc and alcoholic hydrochloric acid, or with zinc dust and acetic acid, he obtained more complex products, some of which it was almost impossible to purify, we decided to try first the action of tin and hydrochloric acid with alcohol upon our dibromdinitrophenylmalonic ester, and for this purpose proceeded as follows. 2 grs. of the dibromdinitrophenylmalonic ester were mixed with alcohol, strong hydrochloric acid, and tin, a piece of platinum foil being used to accelerate the action, and the mixture was kept upon a steam radiator at a temperature of from 50° – 70° until the whole of the malonic compound had disappeared, which usually happened in an hour and a half. The clear solution was poured off from the excess of tin, and, after evaporation to dryness, dissolved again in water, and

* Ann. Chem., ccli. 364.

freed from tin with sulphuretted hydrogen; upon concentrating the filtrate, long needles separated, which varied in color from brown to nearly white. By further concentration of the mother liquors a fresh crop of crystals was obtained, and the precipitate of sulphide of tin must be boiled out several times with water, as the reduction-product is but slightly soluble. As the substance seemed to be decomposed to a certain extent by our attempts to purify it by crystallization, we analyzed some of it without further purification, while other samples were crystallized once more from hot water, allowing the solution to cool *in vacuo* to avoid oxidation by the air. It was dried *in vacuo*, and analyzed with the following results:—

- I. 0.0977 gr. of the substance gave on combustion 0.1224 gr. of carbonic dioxide and 0.0434 gr. of water.
- II. 0.3108 gr. gave on combustion 0.3869 gr. of carbonic dioxide and 0.1128 gr. of water.
- III. 0.1113 gr. of the substance gave 9.8 c.c. of nitrogen at a temperature of 25°.5 and a pressure of 763 mm.
- IV. 0.1010 gr. of the substance treated with argentic nitrate and the precipitate washed with nitric acid and water gave 0.0498 gr. of argentic chloride.
- V. 0.4762 gr. gave 0.2461 gr. of argentic chloride.

	I.	II.	Found.	III.	IV.	V.
Carbon	34.17	33.93				
Hydrogen	4.93	4.03				
Nitrogen				9.84		
Chlorine					12.19	12.77

The free base corresponding to this chloride was next prepared by adding ammoniac hydrate to a strong solution of it, when a white precipitate swimming in a dark green liquid was obtained. It was purified by washing with cold water, in which it is as good as insoluble, until the wash water gave no test for a chloride, then dried *in vacuo*, and analyzed with the following results:—

- I. 0.1690 gr. of the substance gave on combustion 0.2587 gr. of carbonic dioxide and 0.0580 gr. of water.
- II. 0.2021 gr. of the substance gave 23.7 c.c. of nitrogen at a temperature of 24°.5 and a pressure of 768.5 mm.

	I.	Found.	II.
Carbon	41.75		
Hydrogen	3.81		
Nitrogen			13.28

The following comparison shows that the numbers obtained from the analyses of the chloride correspond to those calculated for the formula $C_8H_9BrN_2O_2HCl$ (with the exception of the hydrogen,* which was undoubtedly brought too high by the passing over of a part of the halogen into the sulphuric acid bulbs).

	Calculated for $C_8H_9BrN_2O_2HCl$.	Found.	
Carbon	34.12	34.17	33.93
Hydrogen	3.55	4.93	4.03
Nitrogen	9.95	9.84	
Chlorine	12.61	12.19	12.77

On the other hand, the numbers given by the analyses of the free base indicate a substance containing one molecule less of water.

	Calculated for $C_8H_7BrN_2O$.	Found.	Calculated for $C_8H_9BrN_2O_2$.
Carbon	42.30	41.75	39.17
Hydrogen	3.08	3.81	3.67
Nitrogen	12.34	13.28	11.43

The want of agreement between the percentages of hydrogen† is explained in the same way as in the analyses of the chloride. Otherwise the numbers come as near as could be expected, when it is remembered that the free base was so unstable that we did not dare to purify it except by washing, and that it gradually turned brown even when dry.

In order to harmonize these results and determine the nature of the substances we have found only three hypotheses.

First, and most obvious. The two substances belong to different classes, i. e. one is the chloride of the bromdiamidophenylacetic acid $C_6H_2BrNH_2CINH_2CH_2COOH$; the other is free bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$.

If, on the other hand, the substances belong to the same class, —

Second. They are the bromamidooxindol and its chloride. In this case the chloride must contain one molecule of water of crystallization.

Third. They are bromdiamidophenylacetic acid and its chloride. In this case our analyses of the free base are incorrect.

* The formula $C_8H_{11}BrN_2O_2HCl$ requires 4.23 per cent of hydrogen, and is therefore distinctly too high for Analysis II., and the analysis of the "chloride of the free base" given later. The small amount of substance used in Analysis I. makes the per cent of hydrogen in it of no value.

† The formula $C_8H_9BrN_2O$ requires 3.93 per cent of hydrogen.

If the first of these explanations is the true one, the chloride made by adding hydrochloric acid to the free base would be the chloride of the bromamidooxindol, and therefore different from the original chloride of the bromdiamidophenylacetic acid. To settle this point, we set free the base with ammoniac hydrate from a quantity of the original chloride, and, after washing until free from ammoniac chloride, dissolved it in dilute hydrochloric acid and crystallized it from the slightly acid solution. The general habit of the crystals of the two chlorides (the original one and that made from the free base) was the same, but there were differences in the modifications on the ends of the prisms which made the identity of the two somewhat doubtful; we accordingly analyzed the chloride made from the free base, with the following results:—

0.1853 gr. of the substance gave on combustion 0.2328 gr. of carbonic dioxide and 0.0678 gr. of water.

	Calculated for $C_8H_7BrN_2OHCl$.	Calculated for $C_8H_9BrN_2O_2HCl$.	Found.	Analyses of Original Chloride.	
Carbon	36.43	34.12	34.26	34.17	33.93
Hydrogen	3.04	3.55	4.06	4.93	4.03

There can be no doubt, therefore, of the identity of the two chlorides, and the first explanation must be abandoned.

The second explanation requires that the chloride should contain one molecule of water of crystallization. This point was tested by heating the chloride with the following result:—

0.2517 gr. of the chloride heated for 6 hours at first at 110° , later to 135° , lost 0.0024 gr.

	Calculated for $C_8H_7BrN_2OHClH_2O$.	Found.
Water	6.42	0.95

From this it appears that, if the chloride contains water of crystallization, it does not lose it at 135° . The slight loss of only 2.4 mgrs. could be sufficiently accounted for by the decomposition of the salt, which had turned dark gray on the surface, and for this reason too the heating could not be repeated at a higher temperature.

This result, unfavorable to the second explanation, necessitates the discussion of the third,—that the free base is bromdiamidophenylacetic acid,—which otherwise we should not have thought worthy of consideration. As has been already stated, the analyses of the free base do not agree with this explanation, and in order to adopt it we must assume that the substance had undergone a decomposition sufficient to

raise the carbon 2.58 per cent, an assumption improbable in itself, and not supported by the appearance of the preparation, which had only a slight dirty pink color. This we think is enough to condemn this third explanation, but we add the following considerations, all of which tell strongly in favor of the second, and against the third explanation. (1.) Gabriel and R. Meyer* by the reduction of dinitrophenylacetic acid with tin and hydrochloric acid obtained the paramidooxindol direct, and it does not seem possible that our bromdiamidophenylacetic acid, which differs from theirs only in containing an atom of bromine, should be so much more stable. (2.) Our free base agrees fairly well in properties with the paramidooxindol of Gabriel and R. Meyer. Both are easily oxidized, soluble in hot water or in alcohol, slightly soluble in benzol or carbonic disulphide, the only difference being that our base is nearly insoluble in ether, whereas theirs is soluble in it. The melting points also stand about where we should expect, amidooxindol about 200° , our bromamidooxindol about 212° ; in both cases there was so much blackening that the melting point could not be accurately determined. (3.) Our base (or its chloride) gives the indol reaction, turning a piece of pine wood red if boiled with it and dilute sulphuric acid, or if the wood, after being saturated with a solution of the base, is soaked in strong hydrochloric acid. This seems to us conclusive. The color is rather dull, and appears only after some time; but the objection which might be urged against this argument on this account, that the bromdiamidophenylacetic acid was converted into the bromamidooxindol by treatment with the acids, has no weight, as in the preparation of the original chloride it was most thoroughly exposed to the action of strong hydrochloric acid, both hot and cold; and yet this chloride, as we have shown by the analyses, contained two atoms of hydrogen and one of oxygen more than is required by the chloride of the bromamidooxindol.

These arguments seem to us to prove conclusively that the two substances are bromamidooxindol $C_6H_2BrNH_2(CH_2CONH)$, and its chloride $C_6H_2BrNH_2(CH_2CONH)HCl \cdot H_2O$, in spite of the fact that we could not drive off the water of crystallization from the chloride even at 135° .

Properties of Bromamidooxindol, $C_6H_2BrNH_2(CH_2CONH)$.

As precipitated from its chloride it forms a heavy flocculent white precipitate, which, when examined with the microscope, is seen to be

* Ber. d. ch. G., xiv. 832.

a felt of small white needles, often arranged in fagots or groups like an hour-glass; it is not very stable, changing to a dirty pink on exposure to the air, even when dry. The substance analyzed melted at 212° with a good deal of blackening, but we do not place much reliance on this melting point, as the sample used was a good deal colored. It is almost insoluble in cold, soluble in hot water; soluble in hot alcohol; insoluble or nearly so in ether or chloroform; not freely soluble in benzol or carbonic disulphide, even when hot; freely soluble in hot glacial acetic acid. Sodid hydrate dissolves it, giving a pinkish or pale magenta solution; ammoniac hydrate at first seems to have no action, but on standing the liquid and solid turn dark bluish green; potassic carbonate in aqueous solution does not dissolve it. It seems therefore to have the properties of a phenol. Neither picric acid in benzol solution, nor ferric chloride with an alcoholic solution of the base, produced any change of color. If some of the free base was boiled with dilute sulphuric acid and a piece of pine, the wood was turned a dull orange-red.

As to the constitution of this base, it has been determined by work* done in this laboratory on the bromdinitrophenylmalonic ester that the nitro group, from which the amido group is formed, is in the para position to the carbon side chain. The bromine is probably in the ortho position, since all our work with the tetrabromdinitrobenzol has shown that only three of its atoms of bromine can be replaced easily; and, as the compounds made from this substance are so closely analogous to those prepared from the tribromdinitrobenzol, it is fair to infer that the three symmetrical (meta) atoms of bromine are those which can be removed, and that the fourth more stable atom of bromine is the one in the unsymmetrical (ortho) position; the atom of bromine, therefore, which reduction takes away from the dibromdinitrophenylmalonic ester, would be that in the meta position, and the base would be accordingly *orthobromparamidooxindol*.

Properties of the Chloride of Bromamidooxindol,
 $C_6H_2BrNH_2(CH_2CONH)HClH_2O$.

When crystallized from water, the substance forms needles, or prisms, sometimes as much as a centimeter long and a millimeter thick, which seem to belong to the monoclinic system, and usually have a yellowish color; we think, however, that this color is due to partial oxidation, and that the substance is white when pure. When

* These Proceedings, xxiv. 249, 250.

examined with the microscope, the prisms are found to be arranged in globular radiating groups, and are terminated usually by a single rhombic plane at a not very oblique angle to the long sides of the prism; sometimes a number of other modifying planes are observed, giving a sharp end to the prism. From alcohol it crystallizes in branching needles set at a very acute angle to each other. It melts only at a very high temperature, probably above the range of the mercury thermometer. It is slightly soluble in cold water, freely in hot; soluble in alcohol; slightly soluble in cold benzol, chloroform, or glacial acetic acid, freely soluble in these solvents, when hot; almost insoluble in ether; very soluble in carbonic disulphide. The best solvent for the substance is boiling water. An excess of ammoniacal hydrate throws down from a concentrated solution a heavy precipitate of the free base, which is white, but the liquid turns dark green; potassic carbonate gives a similar precipitate, not soluble in an excess; sodic hydrate in small quantity gives a similar precipitate, but dissolves it when added in larger quantity, giving a reddish solution. It gives a dull orange-red indol reaction with pine wood.